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Polydimethylsiloxane/Glass-Based Composite Elastomer for Thermophysical Applications

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Abstract

The possibility of reducing the thermal conductivity of the composite material based on polydimethylsiloxane by adding hollow glass microspheres as fillers was tested. Based on the data obtained, it can be concluded that a composite material containing microspheres at a concentration of 2.5% has a lower thermal conductivity coefficient by 40%, but also loses adhesion work and transparency in the optical range.

Keywords: Thermal conductivity; Microspheres; Adhesion; Polydimethylsiloxane; Composite material

1. INTRODUCTION

Polydimethylsiloxane (PDMS) is the most widely used silicon-based polymer due to its versatility and attractive properties [1,2]. In particular, PDMS is non-flammable, non-toxic, transparent, odorless, tasteless and colorless. The production of PDMS involves cross-linking in the liquid phase to produce a hydrophobic and mechanically flexible material in the final solid form. This allows you to add various easily customizable fillers (additives) that affect the properties of the resulting material [3,4].

One property that can be modified by fillers in both directions is thermal conductivity. An increase in thermal conductivity may be important when using PDMS as a thermal interface in electronics. There are number of works in which this is ensured by adding various fillers (mostly metallic or carbon-based) [5–8]. However, a reduced thermal conductivity of PDMS may also be in demand, for example, in construction or in the space industry. Possible methods include the formation of pores in the matrix (material) [9], and the introduction of more heat-insulating or heat-reflecting materials into the volume of the material [10]. At the moment, only few works [11–13] are available on reducing thermal conductivity of PDMS by filler addition, which is probably due to the initial relatively low thermal conductivity of PDMS ($\lambda \approx 0.17$ W/m·K) [9].

One of the most efficient heat-insulating material is silica aerogel [6,14–16] having thermal conductivity as low as 0.013–0.04 W/m·K. When used as a filler material, aerogel should be additionally processed to obtain either strongly hydrophobic or hydrophilic properties (depending on matrix composition) in order to prevent the absorption of the liquid from the matrix material during the composite fabrication [6,15,16] that may result in increased thermal conductivity of the composite [6,9,13–17]. Lee et al. [13] reported preparation of PDMS-aerogel composite with the heat conductivity of just 0.018 W/m·K. In their work, aerogel pores were filled with ethanol before mixing with PDMS. After curing at 80 °C, the ethanol was removed from composite by evaporation and diffusion. In spite of the very low heat conductivity of PDMS-aerogel composite, it requires additional preparation and processing steps, which is often unacceptable for fabrication outside the laboratory conditions. Moreover, silica aerogel is relatively expensive and mechanically weak material.

Another perspective silica-based material with low heat conductivity is hollow glass microspheres (HGMs) [10,18]. It is mechanically stronger [19] and more cost-efficient than silica aerogel. Closed structure of the spheres prevents them from being filled with the matrix material [17]. Nevertheless, care should be taken to avoid damaging of HGMs that otherwise may result in opposite effect on heat conductivity [20]. In a recent study by Vlassov et al. [12]

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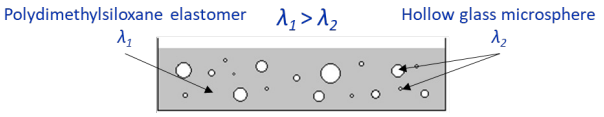

Fig. 1. Schematics representation of the structure of a composite material based on polydimethylsiloxane elastomer filled with hollow glass microspheres (λ_1 and λ_2 denote the average thermal conductivity of polydimethylsiloxane and hollow glass microspheres respectively).

authors prepared PDMS–HGMs composites using commercially available HGMs (Q-CEL 300, Potters) and achieved 31% reduction of thermal conductivity (from 0.16 to 0.11 W/m·K) at 17 wt% HGM content. This is significantly less than results obtained by Lee et al. [13] with aerogel filler, but PDMS–HGMs composite benefits from simplicity of preparation and more user-friendly cost.

In this work, we explore thermal insulation capacity of PDMS–HGM composites further by testing the filler made by Graphite PRO. In addition to thermal conductivity, we measure optical and adhesion properties of the composite.

2. FABRICATION OF COMPOSITE MATERIALS

Solid PDMS was obtained using a set of Sylgard 184 elastomers (Dow Corning, USA), consisting of two liquid components: base and curing agent. The ratio of base and curing agent for mixing, according to the documentation, is 10:1. This set was chosen as the basis (matrix) in many scientific articles [1,2,12,21], which made it a widely used model elastomer. HGM (Graphite PRO, Russia) with a bulk density of 0.19 g/cm^3 were used as a filler. The filler concentration in this work varied from 0 to 10 wt%.

The decrease in thermal conductivity is expected due to the hollow closed structure of the spheres, so that the gas inside is not filled with the matrix material when mixed with PDMS (Fig. 1).

The manufacturing process included several stages:

- Mixing: accurately weighted base, curing agent and HGM as a filler was mixed in a SpeedMixer (TM) DAC 150.1 FVZ mixer for 5 minutes at 3500 rpm, as a result of which the components were evenly mixed throughout the volume;
- Degassing: the solution was poured into a mold and placed in a metal container, in which a low (~30000 Pa) vacuum was created using a pump to remove air from the volume of the solution (the process lasted about 40 minutes);
- Curing: the solution was thermally treated at 140 °C for two hours to accelerate the chemical crosslinking reactions. After this procedure, the sample is completely solid. Samples were cured inside polytetrafluoroethylene form with a sample size of 12×12×3 cm (to conform with

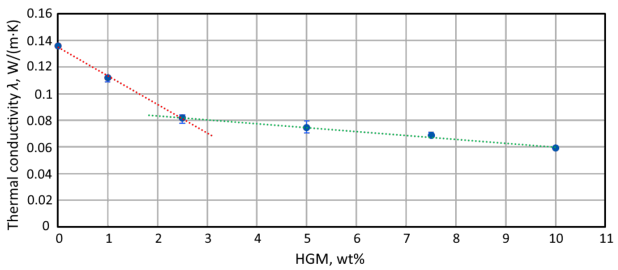

Fig. 2. Graph of the dependence of the thermal conductivity coefficient on the concentration of HGM for fabricated composite materials based on PDMS.

to the requirement of the test equipment for the minimal size of 10×10×3 cm).

Seven samples were made, two of which were pristine (without the addition of fillers), and other samples contained HGM in different percentages (from 0 wt% to 10 wt%). The mass of the sample decreased with increasing the HGM content from 33 g at 0 wt% to 20 g at 10 wt%, which gives 1.65 times decrease in density. In addition, samples with identical composition were prepared in Petri dishes for measurements of adhesive and optical properties.

3. PROPERTIES OF THE COMPOSITE MATERIALS

3.1. Thermal conducting measurement

To measure thermal conductivity, an ITP-MG4 thermal conductivity measuring device (Stroypribor, Russia) was used, which measures thermal conductivity by the method of stationary heat flow with a pressure on the sample of 2.5 kPa (error <2.5%) for 20 minutes. The temperature of the hot edge was $T_H = 30$ °C, the temperature of the cooler was $T_R = 15$ °C, thus creating a temperature gradient $\Delta T = 15$ °C.

The results of thermal conductivity measurements are shown in Figure 2. Thermal conductivity of the pristine PDMS is 0.138 W/m·K, which is similar to the timber. The addition of HGM resulted in significant decrease of thermal conductivity. Two regions can be distinguished on a graph. Faster linear drop in thermal conductivity (from 0.14 to 0.082 W/m·K, or by 39.8%) is observed when HGM content is increased from 0 to 2.5 wt%. Less steep linear decrease is observed from 2.5 wt% to 10 wt% HGM content leading to the total decrease in thermal conductivity down to 0.059 W/m·K (or by 57% relative to the pristine PDMS), which is already between the thermal conductivity of asbestos (0.08 W/m·K [22]) and mineral wool (0.04 W/m·K [23]).

This is a significantly more pronounced effect than the one reported for PDMS-HGM composite by Vlassov

et al. [12] (approximately 22% decrease for 10 wt%). Possible reason may be related to structural integrity of the spheres during the mixing stage. The essential difference between materials used in this work and Ref. [12] is that Vlassov et al. used HGM produced by other maker (Q-CEL 300, Potters). It is possible that HGM used in our study may be more resistant to mechanical damage during the mixing stage. If spheres are broken before curing, they cannot fulfil the heat insulating function. Moreover, broken spheres may increase the thermal conductivity of the composite, as solid glass is a good heat conductor. Another important difference between these studies is the mixing technique. We used dedicated mixer, while Vlassov et al. [12] mixed materials manually. Manual mixing procedure may be more destructive to the spheres. The indirect support for the structural integrity factor as the main reason for the difference between our and Vlassov et al. [12] results is the fact that we observed higher decrease of the PDMS density with added HGM by 1.65 times at 10 wt% in our study versus approximately 1.4 times for the same HGM content in study by Vlassov et al.

3.2. Optical properties measurement

The optical absorption of the samples in the UV/visible region (200–1100 nm) was studied using an Ava-Absorbance UV/visible absorption spectrometer (Avantes, Netherlands), the thickness of the samples did not exceed 3 cm. The results are shown in Figure 3. According to the obtained optical absorption spectra, the sample becomes opaque in the indicated range already at a HGM content of 1 wt%. This is not surprising, as HGM is opaque, and having the low density, they occupy a significant volume fraction in the composite.

3.3. Adhesion properties measurement

Surface properties were studied using experimental equipment (adhesion tester) based on the Johnson-Kendell-Roberts model. For more information on this topic see Ref. [21].

The experiments were carried out with a total probe cycle distance of 12800 microsteps (0.01995 m), probe descent speed of 30.53 microsteps/sec ($4.68 \cdot 10^{-5}$ m/sec), contact delay (before separation) of 2 seconds and delay before starting a new iteration of the loop – 1 second. The probe was a glass ball with a radius of 1.25 cm, and its maximum load on the contact was approximately 6–7 grams (indications on the scales). Before each measurement, the contact surface of the probe was treated with a special anti-dust cloth impregnated with acetone.

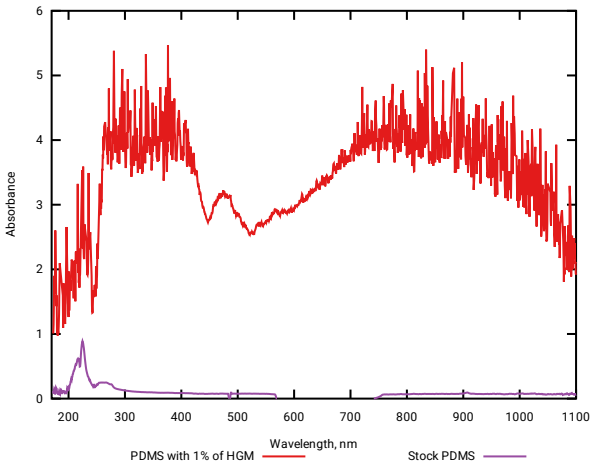

Fig. 3. Absorbance plot of pure PDMS material and composite material based on PDMS with the addition of hollow glass microspheres.

For a composite material based on PDMS with the addition of HGM (not less than 1%), the work of adhesion drops sharply below the detection limit (< $16 \cdot 10^{-5}$ J/m^2). Hence, it can be concluded that the addition of microspheres significantly affects the surface properties of the material. This may be due to the weak adhesive interaction of the "powder" of the hollow glass microspheres with glass and the saturation of the ends of the polymer associated with the HGM, which would otherwise promote adhesive interaction with the glass probe.

4. CONCLUSIONS

In this study, the efficiency of HGM (Graphite PRO, Russia) as a heat-insulating filler for PDMS was tested. PDMS-HGM composites with HGM content up to 10 wt% were prepared. Thermal conductivity decreased from 0.138 W/m·K (similar to timber) for pristine PDMS to 0.059 W/m·K for 10 wt%, which is between mineral wool and asbestos. In total, it gives 56% decrease in thermal conductivity, which is considerably more pronounced than the previously published effect obtained for similar composites using HGM produced by other maker (Potters). While PDMS is optically clear and transparent, addition of HGM changes it to completely opaque at all tested concentrations. Lastly, addition of HGM greatly reduces adhesion of PDMS to the glass ball below detection limit.

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REFERENCES

[1] J.-Y. Kim, K.-S. Jang, *facile fabrication of stretchable electrodes by sedimentation of ag nanoparticles in PDMS matrix*, Journal of Nanomaterials, 2018, vol. 2018, art. no. 4580921.

[2] L. Chen, C. Ma, L. Li, C. Zhu, J. Gu, H. Gao, Z. Zhu, C. Du, T. Wang, J. Xu, G. Chen, *using PDMS plasma cavity SERS substrate for the detection of aspartame*, Journal of Spectroscopy, 2020, vol. 2020, art. no. 4212787.

[3] M.P. Wolf, G.B. Salieb-Beugelaar, P. Hunziker, *PDMS with designer functionalities—Properties, modifications strategies, and applications* // Progress in Polymer Science, 2018, vol. 83, pp. 97–134.

[4] D. Cambié, C. Bottecchia, N.J.W. Straathof, V. Hessel, T. Noël, *Applications of continuous-flow photochemistry in organic synthesis, material science, and water treatment*, Chemical Reviews, 2016, vol. 116, no. 17, pp. 10276–10341.

[5] S. Chowdhury, M. Olima, Y. Liu, M. Saha, J. Bergman, T. Robison, *Poly dimethylsiloxane/carbon nanofiber nanocomposites: fabrication and characterization of electrical and thermal properties*, International Journal of Smart and Nano Materials, 2016, vol. 7, no. 4, pp. 236–247.

[6] H.M. Kim, Y.J. Noh, J. Yu, S.Y. Kim, J.R. Youn, *Silica aerogel/polyvinyl alcohol (PVA) insulation composites with preserved aerogel pores using interfaces between the superhydrophobic aerogel and hydrophilic PVA solution*, Composites Part A: Applied Science and Manufacturing, 2015, vol. 75, pp. 39–45.

[7] Y. Kim, M. Kim, H.-G. Seong, J.Y. Jung, S.-H. Baeck, S.E. Shim, *Roles of silica-coated layer on graphite for thermal conductivity, heat dissipation, thermal stability, and electrical resistivity of polymer composites*, Polymer, 2018, vol. 148, pp. 295–302.

[8] Y.-F. Zhang, Y.-J. Ren, H.-C. Guo, S. Bai, *Enhanced thermal properties of PDMS composites containing vertically aligned graphene tubes*, Applied Thermal Engineering, 2019, vol. 150, pp. 840–848.

[9] N. Al-Khudary, P.Y. Cresson, Y. Orlic, P. Coquet, P. Pernod, T. Lasri, *Measurement of the thermal conductivity of polydimethylsiloxane polymer using the three omega method*, Key Engineering Materials, 2014, vol. 613, pp. 259–266.

[10] J.-H. Hao, Q. Chen, K. Hu, *Porosity distribution optimization of insulation materials by the variational method*, International Journal of Heat and Mass Transfer, 2016, vol. 92, pp. 1–7.

[11] I.-L. Ngo, S. Jeon, C. Byon, *Thermal conductivity of transparent and flexible polymers containing fillers: A literature review*, International Journal of Heat and Mass Transfer, 2016, vol. 98, pp. 219–226.

[12] S. Vlassov, S. Oras, M. Timusk, V. Zadin, T. Tiirats, I.M. Sosnin, R. Lõhmus, A. Linarts, A. Kyritsakis, L.M. Dorogin, *Thermal, mechanical, and acoustic properties of polydimethylsiloxane filled with hollow glass microspheres*, Materials, 2022, vol. 15, no. 5, art. no. 1652.

[13] H. Lee, D. Lee, J. Cho, Y.-O. Kim, S Lim, S. Youn, Y.C. Jung, S.Y. Kim, D.G. Seong, *Super-insulating, flame-retardant, and flexible poly(dimethylsiloxane) composites based on silica aerogel*, Composites Part A: Applied Science and Manufacturing, 2019, vol. 123, pp. 108–113.

[14] D. Ge, L. Yang, Y. Li, J. Zhao, *Hydrophobic and thermal insulation properties of silica aerogel/epoxy composite*, Journal of Non-Crystalline Solids, 2009, vol. 355, no. 52–54, pp. 2610–2615.

[15] S.Y. Kim, Y.J. Noh, J. Lim, N.-H. You, *Silica aerogel/polyimide composites with preserved aerogel pores using multi-step curing*, Macromolecular Research, 2014, vol. 22, no. 1, pp. 108–111.

[16] H.M. Kim, H.S. Kim, S.Y. Kim, J.R. Youn, *Silica aerogel/epoxy composites with preserved aerogel pores and low thermal conductivity*, e-Polymers, 2015, vol. 15, no. 2, pp. 111–117.

[17] M. Vahtrus, S. Oras, M. Antsov, V. Reedo, U. Mäeorg, A. Lõhmus, K. Saal, R. Lõhmus, *Mechanical and thermal properties of epoxy composite thermal insulators filled with silica aerogel and hollow glass microspheres*, Proceedings of the Estonian Academy of Sciences, 2017, vol. 66, no. 4, pp. 339–346.

[18] C. Zhang, L. Qu, Y. Wang, T. Xu, C. Zhang, *Thermal insulation and stability of polysiloxane foams containing hydroxyl-terminated polydimethylsiloxanes*, RSC Advances, 2018, vol. 8, pp. 9901–9909.

[19] A. Trofimov, L. Pleshkov, H. Back, *Hollow glass microspheres for high strength composite cores*, Reinforced Plastics, 2006, vol. 50, no. 7, pp. 44–46, 48–50.

[20] Y. Hu, R. Mei, Z. An, J. Zhang, *Silicon rubber/hollow glass microsphere composites: Influence of broken hollow glass microsphere on mechanical and thermal insulation property*, Composites Science and Technology, 2013, vol. 79, pp. 64–69.

[21] A. Tiwari, L. Dorogin, A.I. Bennett, K.D. Schulze, W.G. Sawyer, M. Tahir, G. Heinrich, B.N.J. Persson, *The effect of surface roughness and viscoelasticity on rubber adhesion*, Soft Matter, 2017, vol. 13, no. 19, pp. 3602–3621.

[22] Q. Yu, *Application of foam glass-ceramic composite thermal insulation material in traditional buildings*, Journal of Chemistry, 2022, vol. 2022, art. no. 9662805.

[23] C.-K. Jeon, J.-S. Lee, H. Chung, J.-H. Kim, J.-P. Park, *A study on insulation characteristics of glass wool and mineral wool coated with a polysiloxane agent*, Advances in Materials Science and Engineering, 2017, vol. 2017, art. no. 3938965.

УДК 536.212.3

Композитный эластомер на основе полидиметилсилоксана/стекла для теплофизических применений

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Аннотация. Была протестирована возможность снижения теплопроводности композитного материала на основе полидиметилсилоксана путем добавления стеклянных полых микросфер. Основываясь на полученных данных, можно заключить, что композитный материал, содержащий микросферы в концентрации 2,5%, имеет меньший коэффициент теплопроводности на 40%, но также утрачивает работу адгезии и прозрачность в оптическом диапазоне.

Ключевые слова: теплопроводность; микросферы; адгезия; полидиметилсилоксан; композитный материал